Molecular Binding Energies[1]

C. Hollister[2] and O. Sinanoğlu[3]

Contribution from the Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut. *Received, August 23, 1965*

Abstract: The effect of the correlation energy on dissociation energies and binding energies of molecules is studied. Molecular correlation energies are obtained semiempirically using only simple molecular orbital calculations and atomic correlation energies. Calculations are done for homonuclear and heteronuclear diatomic molecules and for polyatomic molecules, including some hydrocarbons. The agreement with available experimental data is good. "Experimental" Hartree–Fock molecular orbital energies are predicted. The fractional contribution of correlation to the binding energy is examined and systematic trends are observed, which allow prediction of the binding energy where it is not known.

In the past few years, noteworthy progress in calculation of energies of molecules and atoms has been made. The availability of accurate total energies raises the question of determining binding energies of various types: the dissociation energy, D_e, of diatomic molecules, the energy of atomization of polyatomic molecules, bond-dissociation energies, and energies of fragmentation. Independent calculations of such quantities would be useful for a quantum theoretical basis of bond energies, intramolecular, nonbonded forces, etc.[4a] This is especially important for transient species, radicals, and other species for which the experimental determination of binding energies is difficult. This would also enable one to predict whether a species will exist, as in high-energy fuel and oxidizer research.

Molecular orbital (MO) theory is most widely used for energy calculations. The prototype for this sort of calculation is the Hartree–Fock (H.F.) MO approach. For practical use on larger molecules, we must approximate the H.F. wave function by constructing the MO's as linear combinations of atomic orbitals (LCAO–MO theory) or use a still more approximate method such as the extended Hückel MO (HMO) methods.[5] Sufficient progress has now been made so that these methods are applicable to many systems.[6] Approximate MO treatments are adequate for estimating charge distributions and total energies. However, binding energies are small differences between two large quantities, and in order to estimate them we need to include correlation between electrons, which even the H.F. treatment omits. Fortunately, the correlation energy is insensitive to the exact details of the orbitals.[4,7] Thus, using simple MO's, we can get the correlation energy quite accurately. Theory[4,7] and calculations[8,9] for atomic correlations have shown which effects are physically important. With these results for guidance, we can get molecular correlation energies rather simply.

Two semiempirical methods for estimating molecular correlation energies from atomic data are developed here and applied to molecules of various types, *e.g.*, F_2, C_2N_2, and C_6H_6. For some diatomic molecules, the results have already been compared with H.F. calculations.[10,11] For larger molecules, the results give a sizable portion of the energy of atomization and predict "experimental" H.F. energies to which H.F. calculations may be compared. Systematic trends are observed from which dissociation energies and binding energies may be estimated.

The Effect of Electronic Environment on Correlation

H.F. MO theory treats each electron in a molecule as if it were moving in the average field of all the other electrons. Such a procedure neglects instantaneous collisions between electrons, and this is the source of the energy defect known as the correlation energy. The H.F. wave function is antisymmetric in accordance with the Pauli principle, and this keeps electrons with the same spin apart. However, two electrons with opposite spin may occupy the same space orbital. The repulsion between electrons in the same region of space raises the calculated energy. The correlation part of the wave function has been studied extensively[4,7] and the contribution of pair correlations and three- and many-body correlations to the energy have been examined.[4,8,9] It was found that mainly pair correlations are significant for closed shell systems. The correlation energy, E_{corr}, may be written (for a single determinantal state)

---

(1) This paper is based on the dissertation submitted by C. Hollister in partial fulfillment of the requirements for the Ph.D. degree to Yale University, Sept. 1965.

(2) U. S. Public Health Service Trainee, Grants 748-04 and 748-05, 1963–1965.

(3) Alfred P. Sloan Fellow.

(4) (a) See, for example, O. Sinanoğlu, *Advan. Chem. Phys.*, **6**, 315 (1964). (b) For a review of recent quantum chemical methods and work in the field see O. Sinanoğlu and D. F. Tuan, *Ann. Rev. Phys. Chem.*, **15**, 251 (1964).

(5) For a review, see, for example, K. Fukui in "Modern Quantum Chemistry—Istanbul Lectures, Part I, Orbitals," O. Sinanoğlu, Ed., Academic Press Inc., New York, N. Y., 1965. For a discussion of the relationship of various MO methods, see O. Sinanoğlu, *J. Phys. Chem.*, **66**, 2283 (1962).

(6) See, for example, the ARPA symposium on fuel and oxidizer research, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(7) O. Sinanoğlu, *J. Chem. Phys.*, **36**, 706, 3198 (1962).

(8) O. Sinanoğlu and D. F. Tuan, *ibid.*, **38**, 1740 (1963).

(9) V. McKoy and O. Sinanoğlu, *ibid.*, **41**, 2689 (1964); D. F. Tuan and O. Sinanoğlu, *ibid.*, **41**, 2677 (1964); some pair correlations are also available for second-row atoms: see V. McKoy and O. Sinanoğlu in "Modern Quantum Chemistry—Istanbul Lectures, Part II, Interactions," O. Sinanoğlu, Ed., Academic Press Inc., New York, N. Y., 1965.

(10) C. Hollister and O. Sinanoğlu in "Modern Quantum Chemistry–Istanbul Lectures," ref. 9.

(11) Extensive calculations of H.F. wave functions for diatomic molecules are presently underway at the Laboratory of Molecular Structure and Spectra of the University of Chicago. References to calculations on specific molecules are given in Tables II and III. The "calcd." H.F. results kindly supplied by the Chicago group are tentative and should be treated as such. Values in Tables II and III should be compared with the final H.F. values published.

$$E_{\mathrm{corr}} \cong \sum_{i>j}^{N} \epsilon_{ij} \qquad (1)$$

where ϵ_{ij} is the energy contribution due to the correlation of two electrons in MO spin orbitals i and j, respectively. Qualitatively one can easily see why eq. 1 is a good approximation. The effect of antisymmetry is to surround each electron with a Fermi hole which no electron of the same spin can penetrate. It has been shown[7] that the "fluctuation potential" between a pair of electrons is expected to be appreciable only over a range which is smaller than the extent of the Fermi hole. But with three or more electrons, at least two of them are parallel so that they cannot all get within the range of one another's correlation potentials simultaneously. For a review of the formalism and the manner in which these two-, three- and many-electron effects arise, see ref. 4a.

Each pair correlation may be treated independently. This means molecular or atomic correlation can be built up from individual ϵ_{ij}'s. We must now examine the effect of environment on the pair energies, *viz.*, exclusion effects and the fields of the other electrons. The pair energies may be determined by the variational method.[4a] The variational expression for ϵ_{ij} is

$$\tilde{\epsilon}'_{ij} = [2\langle B(ij), g_{ij}\hat{u}_{ij}\rangle + \langle \hat{u}_{ij}(e_i + e_j + m_{ij})\hat{u}_{ij}\rangle]/[1 + \langle \hat{u}_{ij}, \hat{u}_{ij}\rangle] \qquad (2)$$

with

$$\tilde{\epsilon}'_{ij} \rightarrow \epsilon_{ij} = \langle B(ij), g_{ij}\hat{u}_{ij}\rangle$$

at the minimum and where i and j are the H.F. spin orbitals of the two electrons which are correlating, B is the two-electron antisymmetrizer, $\hat{u}_{ij}$ is the pair function which represents the correlation and is to be determined, e_i is the H.F. operator minus the ith orbital energy, $g_{ij} = 1/r_{ij}$, and m_{ij} is the fluctuation potential. The trial pair function is varied, subject to the conditions

$$\langle \hat{u}_{ij}(\mathbf{x}_i, \mathbf{x}_j), k(\mathbf{x}_i)\rangle_{\mathbf{x}_i} = \int \hat{u}_{ij}(\mathbf{x}_i, \mathbf{x}_j)k(\mathbf{x}_i)\mathrm{d}\mathbf{x}_i = 0 \qquad (3)$$

for all occupied orbitals, k, until a minimum for eq. 2 is found, *i.e.*, until $\delta\epsilon_{ij}[\hat{u}_{ij}] = 0$. The other electrons affect the correlation of a given pair in two ways: the H.F. operator appearing in e_i and e_j contains the average potential of the electrons in all the occupied orbitals, and eq. 3 requires that the pair function be orthogonal to all the occupied orbitals. This orthogonality is indicated by the caret above $\hat{u}_{ij}$ and reflects the "exclusion effect."[12]

Calculations on first-row atoms show[9] that pair energies may be roughly divided into two types: dynamical correlations which are transferable from system to system, and nondynamical correlations which are not. An example of a transferable pair energy is $\epsilon(1s^2)$. One may take the value of $\epsilon(1s^2)$ calculated for the He-like ion of an atom over into the neutral atom, because both types of environmental effects are small. However, $\epsilon(2s)^2$ is not transferable, so that $\epsilon(2s^2)$ determined for the Be-like ion of an atom may not be taken over for use in the neutral atom.[9] In the Be-like ion, $\epsilon(2s^2)$ is almost entirely due to excitations of the 2s electrons to the nearby 2p orbitals (2s and 2p are exactly degenerate in the limit of infinite Z). (For the many references to the $1s^2 2s^2$ case in the literature see ref. 4b.) However, $\hat{u}_{ij}$ must be orthogonal to all occupied orbitals, as given by eq. 3. For Be-like ions, $\hat{u}_{ij}$ will contain all the 2p orbitals, but in the neutral atom which has some of the 2p orbitals occupied, $\hat{u}_{ij}$ cannot contain the occupied 2p orbitals. Thus, $\epsilon(2s^2)$ will decrease as one adds 2p electrons to a Be-like ion. One would expect that the correlation energies of transferable pairs, such as $1s^2$, might be taken over into the molecule without much change. However, nontransferable pairs must be treated differently.

Consider the nitrogen atom (^4S) with the ground-state configuration, $1s^2 2s^2 2p_+^{\alpha} 2p_0^{\alpha} 2p_-^{\alpha}$. $\epsilon(2s^2)$ determined from a configuration interaction (CI) function will be zero as all the 2p orbitals are occupied. Using the LCAO method for nitrogen molecule, one can construct ten space orbitals from the atomic orbitals, 1s, 2s, and 2p. The ground-state configuration of N_2 ($^1\Sigma_g^+$) is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4$, leaving $1\pi_g$ and $3\sigma_u$ unoccupied. One might expect to find some "nondynamical" correlation in N_2 associated with the low-lying unoccupied $1\pi_g$ and $3\sigma_u$ orbitals, which will be analogous to unoccupied 2p orbitals in the atom. To test this idea, a 2 × 2 CI was performed on N_2 using the orbitals determined by Ransil.[13] The pair function chosen was

$$\hat{u}_{ij} = c(2)^{-1/2}[B(\mathrm{rs}) + B(\bar{\mathrm{s}}\bar{\mathrm{r}})] + c'B(\mathrm{pq}) \qquad (4)$$

where

$$\mathrm{r} = 1\pi_{g+}{}^{\alpha},\ \mathrm{s} = 1\pi_{g-}{}^{\beta},\ \bar{\mathrm{r}} = 1\pi_{g+}{}^{\beta},\ \bar{\mathrm{s}} = 1\pi_{g-}{}^{\alpha},\ \mathrm{p} = 3\sigma_u{}^{\alpha},\ \text{and } \mathrm{q} = 3\ \sigma_u{}^{\beta} \qquad (5)$$

The variational coefficients, c and c', were determined using eq. 2. Three calculations were performed, taking (ij) of eq. 2 as combinations of $2\sigma_g$, $3\sigma_g$, and $2\sigma_u$ with α or β spins.

It is always possible to find a unitary transformation, **t**, which will express the localized "core" orbitals in terms of the molecular orbitals (MO's) without changing the energy. The transformation used here is that given by Peters.[14] If there were no mixing in of $2p\sigma$, the transformation would give atomic 2s orbitals exactly since $(\sigma_g 2s)^2(\sigma_u 2s)^2$ will transform to $(2s_a)^2(2s_b)^2$, where a and b number the nuclei. However, **t** including $3\sigma_g$ is approximately equal to **t** for equivalent orbitals, so that the amount of $2p_\sigma$ in the localized orbital (LO) is slight. Thus, $(LO_a)^2$ is very close to $2s_a{}^2$ of the free atom. The pair energy will then transform as[4,7]

$$\epsilon_{\rho\nu} = \langle \sum_{\nu\pm\rho} t_{\rho i}t_{\nu j}B(ij), g_{ij} \sum_{\nu\pm\rho} t_{\rho i}t_{\nu j}\hat{u}_{ij} \rangle \qquad (6)$$

where $\rho\nu$ represent LO^2 and i,j run over $2\sigma_g$, $3\sigma_g$, and $2\sigma_u$. $\epsilon(LO^2)$ per atom in N_2 is computed to be −0.3 e.v. The core energy is lowered by about 0.3 e.v. in the molecule compared to the corresponding core of the free atom. Thus the effect contributes about 0.6 e.v. to the binding energy.

The above calculation indicates the magnitude of the exclusion effect. For more accurate values of the

---

(12) O. Sinanoğlu, *J. Chem. Phys.*, 33, 1212 (1960).

(13) B. J. Ransil, *Rev. Mod. Phys.*, 32, 245 (1960).

(14) D. Peters, *J. Chem. Soc.*, 2003 (1963).

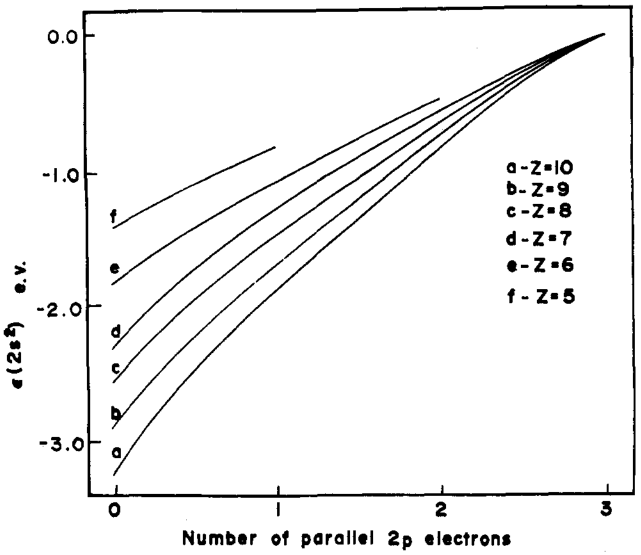


Figure 1. Dependence of ε(2s²) on the occupation of the 2p shell.

correlation energy, CI with more complete H.F. orbitals may be needed. However, a much simpler method, which does not require any molecular H.F. results, suggests itself for estimates.

For the different ionized species of a given atom, one may plot ε(2s²) *vs.* the number of parallel spin p electrons, using values of ε(2s²) given in ref. 9. Figure 1 shows the data for first-row atoms and ions. This allows graphical interpolation to determine ε(2s²) for nonintegral p occupation numbers. Nonintegral p occupation often arises in molecules owing to the displacement of electrons into bonding regions, and the p occupation in the molecule will generally be less than in the corresponding free atom. Such an interpolation for N_2 gives an ε(2s²) per atom of −0.5 e.v., about the same magnitude as that determined by the CI calculation above. Interpolated values are used in the rest of this work where ε(2s²) is required.

Two semiempirical methods for estimating molecular correlation energies from atomic data are described below. Method I uses only the total correlation energy (E_{corr}) of atoms and ions. Total atomic or ionic values of E_{corr} are from Clementi.[15] Method II uses atomic pair correlation energies,[9] modified where necessary by environmental effects. Table I gives values of ϵ_{ij} for first-row atoms and ions. Table I together with Figure 1 [for interpolated values of ε(2s²)] provides all the data necessary for estimating correlation using method II in molecules containing only first-row atoms.[9]

Table I. Pair Correlation Energies for First-Row Atoms

Z	$\epsilon(1s^2)$,[a] e.v.	$\epsilon(1s \rightarrow 2s)$,[b] e.v.	$\epsilon(2s \rightarrow 2p)$,[b] e.v.	$\epsilon(2p_z^2)$,[b] e.v.
3	1.184			
4	1.205	0.058		
5	1.219	0.105	0.379	
6	1.227	0.099	0.579	1.0
7	1.233	0.075	0.680	1.0
8	1.238	0.107	0.780	1.0
9	1.241	0.110	0.762	1.0

[a] Data from ref. 15. [b] Data from ref. 9.

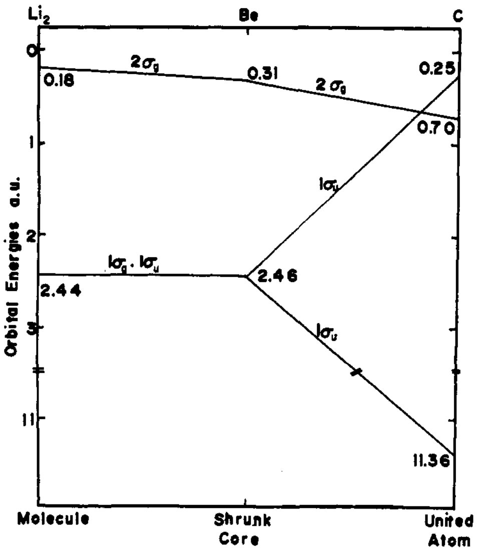


Figure 2a. Orbital energies in united atom, shrunk-core atom[c] and molecule. Li_2 molecule.

Method I. The "Shrunk-Core" Model

In early work, diatomic molecules were studied by considering two limiting atomic cases: the united atom and the separated atoms. MO diagrams[16] were constructed connecting related atomic orbitals of the two atomic limits with the orbitals of the diatomic molecule lying between the two extremes. Historically, this approach developed from H_2^+. The united atom model is reasonable for diatomic hydrides and has been used by Stanton[17] for estimating dissociation and correlation energies of such molecules. The correspondence between MO energies and orbital energies of the united atom is good in the case of hydrides, but large differences occur if both atoms in a diatomic molecule have core electrons. As the molecule contracts until the nuclei unite, we must consider the repulsion of the inner electronic shells of the constituent atoms. Consequently, while the $\sigma_g 1s$ orbital of the molecule goes over, in the united-atom limit, to 1s, and the $\sigma_g 2s$ goes to 2s, the $\sigma_u 1s$ goes to $2p_\sigma$.

An examination of the coefficients in an LCAO treatment of a molecule indicates that the lowest MO's are made up chiefly of atomic core electrons centered about each nucleus; their orbital energies bear little resemblance to the corresponding ones in the united atom. For a general molecule, there are two factors which will affect the orbital energy. The first is the effective nuclear charge seen by the electrons, which will be important mainly for the 1s electrons. The other is the exclusion effect of the inner electrons (resulting in the orthogonality requirements on the orbitals), keeping the outer electrons at a certain distance from the nucleus. In the united-atom model, the innermost electrons see too high an effective *Z* in comparison to what they would see in the molecule if they are centered about their respective nuclei; and since the inner electrons are so tightly bound, they do not exclude the outer electrons from a large enough region of space. A much closer analogy to the mole-

---

(15) E. Clementi, *J. Chem. Phys.*, 38, 2248 (1963); **39**, 175 (1963).

(16) See, for example, C. A. Coulson, "Valence," Oxford University Press, Oxford, 1952.

(17) R. E. Stanton, *J. Chem. Phys.*, **36**, 1298 (1962).

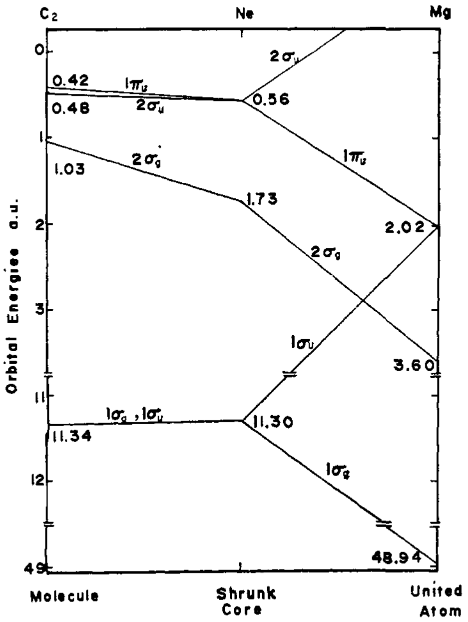


Figure 2b. Orbital energies in united atom, shrunk-core atom, and molecule. C_2 molecule.

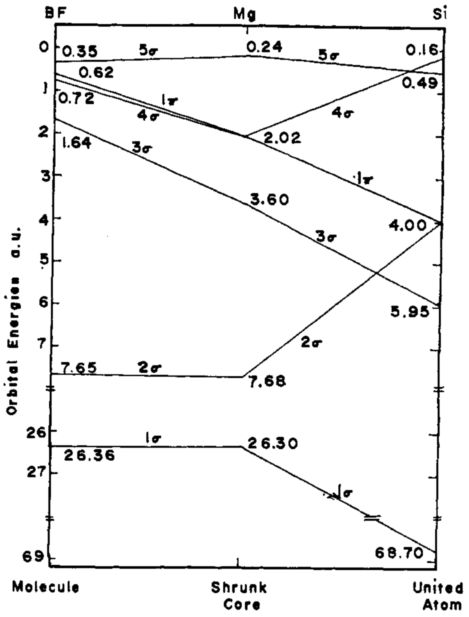


Figure 2c. Orbital energies in united atom, shrunk-core atom, and molecule. BF molecule.

cule is provided by what is called here the "shrunk-core"[18] model. In this model, the core of the resulting atom is very similar to the cores that outer MO's see in the molecule, so that the orbitals and orbital energies of the shrunk-core atom are in much better correspondence to the MO's and their energies. Figure 2 gives MO diagrams for three typical diatomic molecules. The united atom and the shrunk-core atom are shown, but not the separated atoms. The lines connect the MO's with their corresponding AO's in both model atoms. It is clear that the shrunk-core atom does indeed bear a much closer resemblance to the molecule than does the united atom. The same correspondence should apply to the spin-orbital pair correlation energies and to exclusion effects on them. This is important for the cases in which some pair correlation energies are strongly Z-dependent.

An example will make this model clear. Consider the C_2 molecule which has twelve electrons and the symmetry $^1\Sigma_g^+$. An examination of the LCAO coefficients[13] shows that the molecular core has four 1s electrons still centered on their respective nuclei. Thus, the core is essentially $K_a(C^{+4};\ 1s_a{}^2)K_b(C^{+4};\ 1s_b{}^2)$. The remaining eight electrons (in MO's) see a "1s-like" core, at least in the radial direction from the internuclear axis, with a net positive charge about like the sum of two C^{+4} ions. The shrunk-core model now replaces these eight electrons moving in expanded MO's with the outer part of an atom with a similar $1s^2$ core and net charge. The atom is neon. Thus, C_2 is represented by $K_aK_b\mathrm{Ne}(2s^22p^6;\ ^1S)$, and the correlation energy is given by

$$E_{\mathrm{corr}}(C_2) = 2E_{\mathrm{corr}}(C^{+4}) + E_{\mathrm{corr}}(\mathrm{Ne}) - E_{\mathrm{corr}}(\mathrm{Ne}^{+8}) \quad (7)$$

This method is a simple one to use, for only total correlation energies of atoms and ions are required. However, there are two points of some importance to be noted in applying this method, both connected with the exclusion effects discussed in the previous section. First, one must choose the shrunk-core atom to have the appropriate symmetry. For example, the shrunk-core atom for $Be_2(1\Sigma_g^+)$ is carbon. However, the ^3P carbon atom does not have the correct number of paired electrons, so the exclusion effects of the occupied 2p orbitals on the inner shells will not be taken into account properly. One must take an appropriate linear combination of E_{corr} for the ^1D and ^1S states of carbon to produce a situation which resembles that in Be_2. Second, one could, not necessarily with justification, choose for the core of C_2: $K_a'(C^{+2};\ 1s_a{}^22s_a{}^2)K_b'(C^{+2};\ 1s_b{}^22s_b{}^2)$. However, one may not use the value of E_{corr} for the C^{+2} ion directly. As discussed previously (see also ref. 9), the value of $\epsilon(2s^2)$ for the Be-like ion does not take proper account for the exclusion effects of the occupied 2p orbitals, or the corresponding MO's in the molecule, on this nondynamical pair. The same problem does not arise if the core contains only the $1s^2$ electrons since this pair is transferable. If an examination of the LCAO coefficients shows that the best choice of a core contains 2s electrons, one must use the proper values of E_{corr} as calculated in ref. 9 according to the number of outer shell electrons in the molecule. In C_2, for our second choice of core, $\epsilon(K_a';\ C_2)$ is similar to $\epsilon(K_a';\ C\ ^3P)$ or $\epsilon(K_a';\ O\ p_x{}^2p_y{}^2)$. In this work, the cores chosen for all diatomic molecules contain only $1s^2$ electrons.

Note that this method does not include the bond distance explicitly. However, the shrunk-core atom should be approximately the same size as the molecule. This is all that may be necessary. Fischer-Hjalmars[19] recently showed that in the H_2 molecule $E_{\mathrm{corr}}(H_2)$ remains almost constant over a range of bond distances from $R = 0$ to $R = 2R_e$. The same should hold for pair correlations in molecules with many more electrons since the correlation energy is not very sensitive to the details of the orbitals.

---

(18) Not to be confused with the shrunk-core model appearing in the early literature of MO theory.

(19) I. Fischer-Hjalmars in "Modern Quantum Chemistry–Istanbul Lectures," ref. 5.

Table II. Homonuclear Diatomic Molecules

Species[a]		$-\Delta E_{\text{corr}}$, e.v. Method I	Method II	D_e, e.v.[b]	E_{HF}, a.u. Predicted[c]	Calcd.[p]	$\frac{-\Delta E_{\text{corr}}(\text{II})}{D_e}$
Li_2	$^1\Sigma g^+$ [d]	1.26	0.60	1.05[g]	−14.8820	−14.87152[k]	0.57
B_2	$^3\Sigma g^-$ [e]	1.42	1.18	2.90 ± 0.24[h]	−49.1213 ± 0.0088	−49.09088[k]	0.4
C_2	$^1\Sigma g^+$ [d]	3.31	2.99	6.36 ± 0.22[i]	−75.5011 ± 0.0081	−75.40619[l]	0.4
N_2	$^1\Sigma g^+$ [d]	3.20	3.93	9.902[g]	−109.0213	−108.9922[m]	0.4
O_2	$^3\Sigma g^-$ [f]	1.39	1.69	5.178[g]	−149.7470	−149.6659[n]	0.33
F_2	$^1\Sigma g^+$ [d]	2.01	1.82	1.68[j]	−198.8135	−198.7683[o]	1.1

[a] Letters (*d*, *e*, *f*) refer to the limited basis wave function used in method II. [b] All zero-point corrections from ref. 29 unless otherwise specified. [c] Using ΔE_{corr} of method II. Note that error refers only to the error in D_e. [d] See ref. 13. [e] A. A. Padgett and V. Griffing, *J. Chem. Phys.*, **30**, 1286 (1959). [f] G. L. Malli and P. E. Cade, unpublished results. [g] See ref. 29. [h] G. Verhaegen and J. Drowart, *J. Chem. Phys.*, **37**, 1367 (1962). [i] L. Brewer, W. T. Hicks, and O. H. Krikorian, *ibid.*, **36**, 182 (1962); E. A. Ballik and D. A. Ramsay, *Astrophys. J.*, **137**, 84 (1963) [G_0]. [j] R. Iczkowski and J. Margrave, *J. Chem. Phys.*, **30**, 403 (1959). [k] J. B. Greenshields, to be published. [l] P. E. Cade, K. D. Sales, A. C. Wahl, and C. C. J. Roothaan, to be published. [m] P. E. Cade, W. Huo, and C. C. J. Roothaan, to be published. [n] G. L. Malli and P. E. Cade, to be published. [o] A. C. Wahl, *J. Chem. Phys.*, **41**, 2600 (1964). [p] See ref. 11.

Table III. Diatomic Hydride Molecules

Species[a]		$-\Delta E_{\text{corr}}$, e.v. Method I	Method II	D_e, e.v.[b]	E_{HF}, a.u. Predicted[c]	Calcd.[l]	$\frac{-\Delta E_{\text{corr}}(\text{II})}{D_e}$
LiH	$^1\Sigma^+$ [d]	1.88	0.93	2.515[f]	−7.9910	−7.98687[j]	0.37
BH	$^1\Sigma^+$ [d]	1.46	0.80	3.14 ± 0.4[g]	−25.1150 ± 0.0147	−25.02906[j]	0.25
CH	$^2\Pi$ [e]	1.68	1.21	3.64[h]	−38.2779	−38.27935[j]	0.33
NH	$^3\Sigma^-$ [e]	1.90	1.35	3.9 ± 0.5[g]	−54.9579 ± 0.0184	−54.97806[j]	0.33
OH	$^2\Pi$ [e]	1.79	1.45	4.68 ± 0.2[g]	−75.4280 ± 0.0074	−75.42083[j]	0.27
HF	$^1\Sigma^+$ [d]	1.87	1.55	6.06 ± 0.2[g,i]	−100.0751 ± 0.0074	−100.07030[k]	0.25

[a] Letters (*d*, *e*) refer to the limited basis set wave function used in method II. [b] All zero-point corrrections from ref. 29 unless otherwise specified. [c] Using ΔE_{corr} of method II. Note that error refers only to the error in D_e. [d] See ref. 13. [e] M. Krauss, *J. Chem. Phys.*, **28**, 1021 (1958). [f] R. Velasco, *Can. J. Phys.*, **35**, 1204 (1957). [g] See ref. 29. [h] See ref. 28. [i] See ref. 29; G. A. Kuipers, D. F. Smith, and A. H. Nielsen, *J. Chem. Phys.*, **25**, 275 (1956) [G_0]. [j] P. E. Cade, W. Huo, and C. C. J. Roothaan, to be published. [k] K. D. Sales, P. E. Cade, and A. C. Wahl, to be published. [l] See ref. 11.

Table IV. Heteronuclear Diatomic Molecules

Species[a]	$-\Delta E_{\text{corr}}$, e.v. Method I	Method II	D_e, e.v.[b]	E_{HF}, a.u., predicted[c]	$\frac{-\Delta E_{\text{corr}}(\text{II})}{D_e}$
CO $^1\Sigma^+$ [d]	2.36	2.45	11.242[g]	−112.8211	0.23
BF $^1\Sigma^+$ [d]	1.21	1.65	8.58 ± 0.5[g]	−124.1931 ± 0.0184	0.2
BeO $^1\Sigma^+$ [e]	2.00	1.66	6.66 ± 0.1[h]	−89.5662 ± 0.0037	0.25
LiF $^1\Sigma^+$ [d]	1.83	1.33	5.99 ± 0.5[i]	−107.0133 ± 0.0184	0.25
NO $^2\Pi$ [f]	2.20	2.96	6.605[j]	−129.3443	0.4

[a] Letters in this column refer to the limited basis wave function used in method II. [b] All zero-point corrections from ref. 29 unless otherwise specified. [c] Using ΔE_{corr} of method II. Note that error refers only to the error in D_e. [d] See ref. 13. [e] M. Yoshimine, *J. Chem. Phys.*, **40**, 2970 (1964). [f] H. Brion, C. Moser, and M. Yamazaki, *ibid.*, **30**, 673 (1959). [g] See ref. 29. [h] W. A. Chupka, J. Berkowitz, and C. F. Giese, *J. Chem. Phys.*, **30**, 827 (1959). [i] See ref. 29; R. Braunstein and J. W. Trischka, *Phys., Rev.*, **98**, 1021 (1955) [G_0]. [j] See ref. 28.

Tables II, III, and IV give values of ΔE_{corr} calculated by this method. ΔE_{corr} is defined by

$$\Delta E_{\text{corr}} = E_{\text{corr}}(\text{molecule}) - E_{\text{corr}}(\text{atoms}) \quad (8)$$

and is the quantity of interest in examining the dissociation energy. Values of atomic and ionic correlation energies have been taken from Clementi.[15]

Method II. "Pair Populations" Method

Method I may only be used for diatomics and certain small polyatomic hydrides. A more generally applicable method is desirable. An "atoms-in-molecules"[20] type of model might be appropriate where dealing with the correlation energy alone, since the fluctuation potential is short range in character making it a "local" property. For a ground-state molecule (closed shell or single determinantal state),[9,22] eq. 1 gives the correlation energy approximately as the sum of the MO pair correlations. In the LCAO–MO approximation, this sum can be expressed as a sum of inter- and intraatomic pair correlations. Though there seem to be several ways of relating molecular correlations to atomic data and of dealing with the overlap charge regions, only one of these ways is developed here into a method capable of useful results.

The starting point will be a minimal basis set LCAO–MO wave function. This means that the basis set used is limited to those atomic orbitals occupied in the free atom, and the atomic orbitals are usually Slater-type orbitals (STO's). Let us examine the approximate wave function by means of LCAO–MO

---

(20) The "atoms-in-molecules" approach was developed by Moffitt[21] and others. They dealt with the *total* energy of the molecule. The H.F. potential changes considerably going from atoms to the molecule, and the long-range character of the H.F. potential is the source of drastic distortion of atoms in the molecule.

(21) W. Moffitt, *Proc. Roy. Soc.* (London), **A210**, 245 (1951); *Rept. Progr. Phys.*, **17**, 173 (1954). For a review of later work see, *e.g.*, R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, Inc., New York, N. Y., 1963.

(22) H. J. Silverstone and O. Sinanoğlu in "Modern Quantum Chemistry–Istanbul Lectures," ref. 9.

population analysis.[23] Consider a normalized MO in a diatomic molecule

$$\varphi_i = c_a\chi_a + c_b\chi_b \tag{9}$$

where χ_a and χ_b are individually normalized AO's (and may be linear combinations of STO's) on centers *a* and *b*, respectively. The total number of electrons, *N*, in this MO is given by

$$N(\varphi_i)^2 = N(c_a^2 + 2c_ac_b S_{ab} + c_b^2) = N \tag{10}$$

where

$$S_{ab} = \int\chi_a(1)\, \chi_b\,(1)\mathrm{d}v_1$$

The first term in eq. 10 represents the net population on atom *a* and gives a measure of the time the electrons spend there. The second term represents the overlap population and gives a measure of the time the electrons spend in the bonding region. The overlap population is usually[23] divided equally between centers. The sum of the net and overlap populations, in the *i*th MO, on center *a*, gives the gross atomic population

$$n(a_i) = c_a^2 + c_ac_bS_{ab} \tag{11}$$

The sum over the MO's of the gross populations, $n(a_i)$, yields the total gross atomic population for a given AO.

Those populations representing sums over all MO's are invariant[24] with respect to any orthogonal transformation among the occupied LCAO–MO's in a given configuration. The gross atomic population divides the electrons present among the AO's and takes into account, through the overlap populations, the distribution of electrons between different centers. One should then be able to use atomic pair correlation energies, taken in the fractions prescribed by the population analysis, to compute the molecular correlation energy.

Consider the C_2 molecule. Population analysis of the minimal basis set LCAO–MO wave function[13] gives, for each atom[25]: $1s^{2.000}2s^{1.670}2p_z^{0.329}2p_\pi^{2.000}$. A plausible assumption is that, in singlet molecules and closed shells, these populations represent paired electrons; *i.e.*, that there are half as many pairs of electrons in each AO as the MO pair is apportioned *between* the two centers. Then contributions from distributions when the α spin electron is all on center *a*, while the β spin electron is all on center *b* do not become explicit.

Note that in C_2 some of the 2s electrons have been promoted to 2p. Thus, under the pair populations assumption, there are 1.164 *pairs* of 2p electrons, while in the free atom there are none. $|\epsilon(2s^2)|$ is expected to increase owing to nearby unoccupied orbitals, and to the fact that the fractional 2p occupation (of parallel spin p electrons) will often decrease. Atomic pair correlation energies are taken from Figure 1 and Table I.

By comparing the gross atomic population to the populations in the free atom, ΔE_{corr} may be written down directly

$$\Delta E_{\text{corr}} = 2[0.835\epsilon(2s^2)_{\text{molecule}} - \epsilon(2s^2)_{\text{atom}} + \frac{(1.67 - 2)}{2}\epsilon(1s^2 \rightarrow 2s^2) + 0.1645\epsilon(2p_z^2) + \epsilon(2p\pi^2) + \frac{(1.67 \times 2.329 - 4)}{4}\epsilon(1s^22s^2 \rightarrow 2p^2)] \tag{12}$$

Note that in eq. 12 the free-atom value of the correlation energy of a doubly occupied pair such as $\epsilon(1s^2)$ or $\epsilon(2p_z^2)$ simply gets multiplied by the difference of molecular and free-atom pair populations, if it can be assumed to be transferable. For $\epsilon(2s^2)$ different molecular and atomic values must be used as discussed above. Interorbital correlations are obtained by first finding the value for one orbital of each type, each with random spin, and then multiplying this by the number of each kind of electron as given by the population analysis. For example, for the 2s → 2p case,[26] atomic data[9] give directly the value of $\epsilon(1s^22s^2 \rightarrow 2p^2)$ for carbon. Assuming $\epsilon(1s^22s^2 \rightarrow 2p^2) \cong \epsilon(2s^2 \rightarrow 2p^2)$. the random spins value of $\epsilon(2s \rightarrow 2p)$ is one-fourth of this. In the "molecular atom" there are 2.33 random-spin 2p electrons and 1.67 2s electrons. Thus the 2s → 2p correlation in the molecule, per atom, is: $(1.67 \times 2.33/4)\epsilon(2s^2 \rightarrow 2p^2)$. Using the values of the pair correlations[9] we find

$$\Delta E_{\text{corr}} = 2[(0.835 \times 1.1) - 0.457 - (0.165 \times 0.39) + 0.1645 + 1.0 - (0.028 \times 2.317)] = 2.99\text{ e.v.} \tag{13}$$

The arithmetic is written out in order to show the contribution of each effect to the binding energy. This method is very easily carried out for any size molecule so long as a reasonable set of LCAO–MO coefficients is available.

Results

Values of ΔE_{corr} computed by both methods are given in Tables II through VI. The "shrunk-core" model was used only for diatomic molecules and small polyatomic hydrides. Also tabulated are experimental values of the binding energy (B.E.) and calculated nonempirical H.F. energies for the molecules where available. ΔE_{corr}(exptl.) is defined as

$$\Delta E_{\text{corr}}(\text{exptl.}) = D_e - E_{\text{HF}}(\text{molecules}) + E_{\text{HF}}(\text{atoms}) \tag{14}$$

The predicted "experimental" H.F. energies were computed as

$$E_{\text{HF}}(\text{molecules}) = E_{\text{HF}}(\text{atoms}) - \Delta E_{\text{corr}} + \text{B.E.} \tag{15}$$

where ΔE_{corr} from method II was used and ΔE_{rel}, the difference in molecular and atomic relativistic energy corrections, was assumed to be small. Finally, the fractional contribution of ΔE_{corr} to the binding energy, ΔE_{corr}/B.E., is given where, again, ΔE_{corr} from method II was used.

Diatomic Molecules. An examination of Tables II–VI shows that the two methods developed here, although they approach the idea of a molecule from two entirely different points of view, give consistent results in most

---

(23) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(24) C. Scherr, *ibid.*, **23**, 569 (1955).

(25) S. Fraga and B. J. Ransil, *ibid.*, **34**, 727 (1961).

(26) This correlation is not completely dynamical. In nonclosed shell states it contains some "semiinternal" correlation (see ref. 22) from mixing such as 2s2p → 2p′3d. Thus, it changes somewhat from system to system.

Table V. Small Polyatomic Molecules

Species[a]	$-\Delta E_{corr}$, e.v. Method I	$-\Delta E_{corr}$, e.v. Method II	B.E., e.v.[b]	E_{HF}, a.u., predicted[c]	$-\Delta E_{corr}(II)$ / B.E.
HCN [d]	4.01	3.33	13.53[o]	−92.9644	0.25
CO_2 [e]		3.99	16.869[o]	−187.7807	0.24
H_2O [f]	3.67	2.51	10.08[o]	−76.0876	0.25
NH_2 [g]	3.69	2.62	8.2 ± 0.5[p]	−55.7060 ± 0.0191	0.32
NH_3 [h]	5.58	3.55	13.57[q]	−56.2692	0.26
CH_4 [i]		3.69	18.18[r]	−40.2212	0.2
C_3 [j]		3.74	14.12 ± 0.22[s]	−113.4473 ± 0.0081	0.26
C_4 [k]		3.80	19.25 ± 0.5[t]	−151.3223 ± 0.0191	0.2
O_3 [l]		4.74	6.818[o]	−224.5046	0.7
C_2N_2 [m]		5.28	21.7 ± 0.6[r]	−187.7826 ± 0.0220	0.24
$H_2C{=}O$ [n]		3.74	16.24[o]	−114.0309	0.23

[a] Letters in this column refer to the limited basis wave function used in method II. [b] All zero-point corrections from G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., New York, N. Y., 1945, unless otherwise specified. [c] Using ΔE_{corr} of method II. Note that error refers only to the error in B.E. [d] A. D. McLean, *J. Chem. Phys.*, **37**, 627 (1962). [e] See ref. 33. [f] F. Ellison and H. Shull, *J. Chem. Phys.*, **23**, 2348 (1955). [g] J. Higuchi, *ibid.*, **24**, 535 (1956). [h] See ref. 27. [i] B. J. Woznick, *J. Chem. Phys.*, **40**, 2860 (1964). [j] E. Clementi, *ibid.*, **34**, 1468 (1961). [k] E. Clementi, *J. Am. Chem. Soc.*, **83**, 4501 (1961). [l] See ref. 31. [m] E. Clementi and A. D. McLean, *J. Chem. Phys.*, **36**, 563 (1962). [n] P. L. Goodfriend, F. W. Birss, and A. B. F. Duncan, *Rev. Mod. Phys.*, **32**, 307 (1960). [o] G. N. Lewis and M. Randall, "Thermodynamics," revised by K. S. Pitzer and L. Brewer, McGraw-Hill Book Co., Inc., New York, N. Y., 1961. [p] T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press Inc., New York, N. Y., 1953. [q] S. R. Gunn and K. G. Green, *J. Phys. Chem.*, **65**, 779 (1961). [r] See ref. 29. [s] L. Brewer and J. L. Engelke, *J. Chem. Phys.*, **36**, 992 (1962). W. Weltner and D. McLeod, *ibid.*, **40**, 1305 (1964) [G_0]. [t] J. Drowart, R. P. Burns, G. de Maria, and M. G. Inghram, *ibid.*, **31**, 1131 (1959). This is D_0 as there is no spectroscopic data avail-to determine G_0.

Table VI. Larger Molecules

Species[a]	$-\Delta E_{corr}$, e.v. Method II	B.E.,[b] e.v.	E_{HF}, a.u., predicted	$-\Delta E_{corr}$/ B.E.
$HCCH$[c]	2.64	18.600	−76.9638	0.16
$HBNH$[d]	3.48			
H_2CCH_2	4.00	27.044	−78.2242	0.14
H_2BNH_2	4.35			
H_3BNH_3	5.05			
H_2CCCH_2	4.87	30.38	−116.0034	0.14
H_2BNCH_2	4.98			
H_2BCNH_2	5.08			
H_2CBNH_2	5.62			
Benzene	8.42	61.084 ± 0.028	−231.0672 ± 0.0010	0.13
Borazine	10.04			

[a] Letters in this column refer to the wave function used in method II. [b] All dissociation energies from G. N. Lewis and M. Randall, "Thermodynamics," revised by K. S. Pitzer and L. Brewer, McGraw-Hill Book Co., Inc., New York, N. Y., 1961. All zero-point corrections from G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., New York, N. Y., 1945. [c] See ref. 33. [d] This and all following molecules were treated using intermediate unpublished results kindly supplied by Dr. R. Hoffmann. See ref. 32.

cases. The agreement between the molecular H.F. energies predicted here and those calculated at the University of Chicago[11] is good. For almost all cases the values are within 1 e.v. The trends exhibited by the fractional contribution of ΔE_{corr} to D_e are consistent with what is known about the correlation energy. For multiply bonded homonuclear diatomics, this fraction is between 0.33 and 0.4. For singly bonded molecules, the fraction is greater than 0.5 except for B_2 which is a triplet. This is to be expected as the H.F. treatment takes into account "Fermi correlations" between parallel spin electrons and where Fermi correlation is large, coulombic correlation is small. In heteronuclear diatomics the fractions are somewhat less, falling between 0.25 and 0.35 for hydrides and between 0.2 and 0.4 for the others. The polarity of a heteronuclear bond increases the contribution of other factors to the binding energy and, thus, decreases the per cent contribution from the correlation energy.

Small Polyatomic Molecules. Comparison of the two methods developed here given in Table V for polyatomic hydrides shows that the agreement is not as good as for diatomics. This is not surprising as the approximation of a single center being seen by the outer electrons will naturally become poorer in polyatomic molecules, even if the other centers are all hydrogens. Moccia[27] has recently estimated the H.F. energy of H_2O, NH_3, and CH_4 independently, including relativistic corrections. In all cases, his estimates are within 1 e.v. of the values predicted here. The fractional contribution of ΔE_{corr} to B.E. falls between 0.2 and 0.3 for most of the small polyatomics considered (Table V). Although we have no independent estimates of the molecular H.F. energies for polyatomics other than hydrides, let alone calculated values, these fractions would appear to be consistent with the trends noted in diatomics.

Larger Molecules. Table VI contains results for some hydrocarbons and their boron–nitrogen analogs. The fractional contribution of ΔE_{corr} to B.E. is seen to be about constant in those cases where the binding energy is available.

Isoelectronic Series. In Table VII we have grouped results for some isoelectronic series and other related molecules for ease of reference. The two series of

(27) R. Moccia, *J. Chem. Phys.*, 40, 2176 (1964).

diatomics isoelectronic with N_2 and C_2 show a marked decrease in the contribution of ΔE_{corr} to the binding energy upon the introduction of any polarity, and a slower decrease after that. For the hydrides isoelectronic with HF and OH, all values of a given series fall within 5% of one another. This is also true for the series of molecules related to OH and NH by successive addition of hydrogen atoms.

Table VII

Species	$-\Delta E_{corr}$, e.v. Method II	B.E., e.v.	$-\Delta E_{corr}$/B.E.
C_2	2.99	6.36 ± 0.2	0.4
BeO	1.66	6.66 ± 0.1	0.25
LiF	1.33	5.99 ± 0.5	0.25
N_2	3.93	9.902	0.4
CO	2.45	11.242	0.23
BF	1.65	8.58 ± 0.5	0.2
HF	1.55	6.06 ± 0.2	0.25
H_2O	2.51	10.08	0.25
NH_3	3.55	13.57	0.26
CH_4	3.69	18.18	0.2
OH	1.45	4.68 ± 0.2	0.27
NH_2	2.62	8.2 ± 0.5	0.32
OH	1.45	4.68 ± 0.2	0.27
H_2O	2.51	10.08	0.25
NH	1.35	3.9 ± 0.5	0.3
NH_2	2.62	8.2 ± 0.5	0.32
NH_3	3.55	13.57	0.26

Discussion

Lithium Molecule. Table II shows that Li_2 is an exception to the generally good agreement between methods I and II for diatomics. Population analysis[25] of an LCAO-MO wave function[13] shows that the binding in Li_2 is due almost entirely to the 2s electrons. In method I, $\epsilon(2s^2)$ of Be ($Z = 4$) is used in computing ΔE_{corr}, while in method II, $\epsilon(2s^2)$ of Li^- ($Z = 3$) is used. However, $\epsilon(2s^2)$ is strongly Z-dependent,[4b] so that a sizable discrepancy appears. In other molecules, however, binding is due largely to the 2p electrons, with E_{corr} almost independent of Z, and the 2s electrons are chiefly nonbonding.

Carbon and Oxygen Molecules. There is a rather large discrepancy (2.6 and 2.2 e.v., respectively) between the predicted and calculated H.F. energies for C_2 and O_2. It is not clear just what gives rise to this. While it seems unlikely that the calculated values[11] are as 1.5 e.v. from the true H.F. energy, the fractional contribution of the reported H.F. energy to D_e is anomalously low, especially for C_2 (about 12%). The trends found here in the fractional contribution of ΔE_{corr} to D_e are consistent with what is known about the correlation energy. We will tentatively assume that the H.F. limit has not yet been reached in these two cases. Only for N_2 and F_2 have absolutely final production runs for the H.F. wave function been made as of this writing. In method II the correlation energy is taken as the sum of approximate pair energies. The predicted H.F. energy should be lower than, or equal to, that calculated, since nonempirical H.F. calculations are carried out by minimization, and the experimental H.F. minimum is not known beforehand; in fact, it is for all the cases treated here.

Nitrogen Molecule. The desirability of having ΔE_{corr} even approximately is strikingly shown in the case of N_2. For many years there was considerable controversy regarding $D_e(N_2)$. From spectroscopic data, two choices were possible. Herzberg[28] and others held the value of 7.5 e.v., while Gaydon[29] supported a value of 9.9 e.v. This controversy has since been resolved in favor of the latter. Note, however, that the H.F. contribution to D_e is only about 5.5 e.v. and thus both values of D_e would still be possible. With the addition of ΔE_{corr} (= 4 e.v.), it is clear that the larger value of D_e must be the correct one.

Ozone Molecule. The fractional contribution of ΔE_{corr} to the binding energy of O_3 is 0.7, in contrast to other small polyatomics with values between 0.2 and 0.3. It is impossible to decide if this large value is real for the reasons discussed below. Mulliken[30] has discussed the choice of basis sets for LCAO-MO calculations. The population analysis can give very different results for different choices of basis set. We have consistently chosen the same type of approximate wave function so that comparisons could be made. For most of the molecules treated here, the wave functions used were constructed from STO's occupied in the free atoms. However, the only wave function available for ozone[31] is made up of atomic H.F. orbitals, and the 1s electrons are not included explicitly. Population analysis shows that there is very little 2s-2p promotion in the ozone molecule with this wave function. This tends to increase ΔE_{corr} (see eq. 12 and 13, where the third and last terms are negative owing to decreased 2s population). Fischer-Hjalmars[31] remarks that 2s-2p promotion increases when STO's are used, but she does not indicate by how much, nor whether 1s electrons are included. No similar treatments are available for other molecules, so one cannot determine the effect of using H.F. AO's and of excluding 1s electrons on the gross atomic populations.

Larger Molecules. The wave functions for the molecules given in Table VI are not of the LCAO-MO variety, but were determined using Hoffmann's[32] extended Hückel method. There is also available an LCAO-MO wave function[33] for acetylene, so that one may compare populations from the two wave functions. There is less 2s-2p promotion in the Hückel wave function and a somewhat larger hydrogen population. The 2p population is, thus, considerably smaller than from the LCAO-MO wave function. In the case of acetylene, the decreased contribution of the 2p electrons is almost cancelled by the increased contribution from the 2s electrons (see eq. 12 and 13). The difference in ΔE_{corr} is only 0.3 e.v. However, there is no guarantee that this cancellation will also occur in the larger molecules. One may probably predict heats of formation with a fair amount of confidence, however, since all the molecules are treated in the same approximation. The fractional contribution of ΔE_{corr} to the binding energy is about constant in those cases where experimental values are available. No reliance should be

---

(28) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1950.

(29) A. G. Gaydon, "Dissociation Energies," Chapman-Hall, Ltd., London, 1953.

(30) R. S. Mulliken, *J. Chem. Phys.*, **36**, 3428 (1962).

(31) I. Fischer-Hjalmars, *Arkiv Fysik*, **11**, 529 (1957).

(32) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2474 (1964).

(33) A. D. McLean, *ibid.*, **32**, 1595 (1960).

placed on the magnitude of ΔE_{corr} with the limited amount presently known about the wave functions of these large systems.

Limitations and Extensions. The methods given here are applicable to closed shell or single determinantal states. This includes the ground states of most molecules. The extension of these methods to nonclosed shell states is being studied. This will allow the treatment of potential energy surfaces as well as of electronic spectra.

For larger molecules, the approximations involved in the "pair populations" method need further basic study. The application of this method is limited by the need for simple MO wave functions and atomic pair correlation energies. The accuracy of pair correlation energies may improve. It is encouraging that ΔE_{corr} may be obtained quite easily from simple MO wave functions. This, of course, increases the applications of H.F. calculations. The agreement with available H.F. results is good, and calculations on larger systems would help test both these correlation methods and various ways of calculating approximate H.F. MO's.

Acknowledgments. This work was supported in part by a grant from the National Science Foundation. Thanks are due to Dr. J. B. Greenshields and, particularly, to Dr. Paul E. Cade for providing many H.F. results prior to publication.

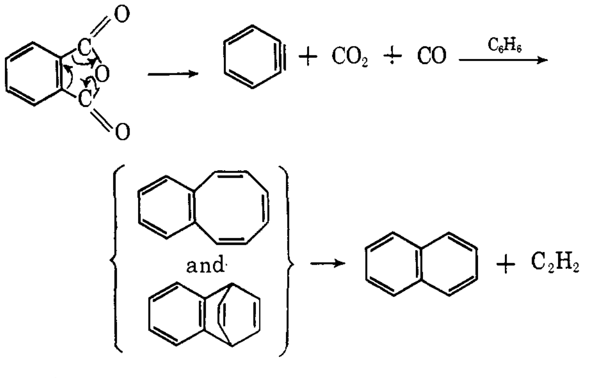
Pyrolysis of Deuterated Benzene

Ellis K. Fields[1a] and Seymour Meyerson[1b]

Contribution from the Research Department, Amoco Chemicals Corporation, and the Research and Development Department, American Oil Company, Whiting, Indiana. *Received September 15, 1965*

Abstract: Pyrolysis of benzene-d_1 and analysis of the pyrolysate revealed a considerable amount of scrambling of protium and deuterium in the recovered benzene. The isotopic composition of the biphenyl produced corresponded closely to that of the benzene that had undergone exchange. The data are best explained by formation of an intermediate phenylcyclohexadiene.

Benzyne, generated by pyrolysis of phthalic anhydride in benzene at 690°, reacts with the benzene to give mainly naphthalene and biphenyl.[2a] To elucidate the mechanism, we pyrolyzed a solution of phthalic anhydride in benzene-d_1. Naphthalene probably forms by 1,2- and 1,4-addition of benzyne to benzene, followed by elimination of acetylene.[2b]



(1)

Barring an appreciable isotope effect, two-thirds of the naphthalene should contain a deuterium atom and one-third only protium. Biphenyl arises in two ways: insertion of benzyne into a C–H bond of benzene and pyrolysis of benzene. Biphenyl from benzyne insertion should form with retention of the deuterium atom; biphenyl from benzene pyrolysis should—again ignoring any isotope effect—be d_0, d_1, and d_2 on the statistical basis of losing two, one, or zero deuterium atoms from a total of twelve protiums and deuteriums in the over-all reaction of two benzene molecules. The amount of biphenyl-d_1 in excess of an appropriately calculated value would presumably be due to the benzyne insertion reaction. Actual results are shown in Table I.

Table I. Products from Pyrolysis of Phthalic Anhydride in Benzene-d_1

Mass	No. of D atoms	Rel. abundance Calcd.[a]	Rel. abundance Found
		Naphthalene	
128	0	37.0	38.6
129	1	63.0	49.9
130	2	0	10.0
131	3	0	1.5
		Biphenyl	
154	0	...	8.2
155	1	...	35.4
156	2	...	44.8
157	3	...	8.8
158	4	...	0.9
159	5	...	0.1

[a] On the basis of 94.5% benzene-d_1 and 5.5% benzene-d_0 used as starting material.

The observed naphthalene results do not agree well with those calculated. Further, a considerable amount

---

(1) (a) Amoco Chemicals Corp.; (b) American Oil Company.

(2) (a) E. K. Fields and S. Meyerson, *Chem. Commun.* (London), 474 (1965). The low-temperature reaction of benzyne from *o*-benzenediazoniumcarboxylate with benzene is discussed by R. G. Miller and M. Stiles, *J. Am. Chem. Soc.*, **85**, 1798 (1963); (b) R. F. C. Brown and R. K. Solly, *Chem. Ind.* (London), 181 (1965).